AD-A281 679

Naval Research Laboratory

Washington, DC 20375-5320

NRL/MR/6110--94-7492

Development of a Dosimeter System for Unsymmetrical Dimethylhydrazine, Monomethylhydrazine and Hydrazine

SUSAN L. ROSE-PEHRSSON

Chemical Dynamic and Diagnostics Branch
Chemistry Division

KAREN P. BRENNER

Geo-Centers, Inc.,
Fort Washington, MD

July 5, 1994

Approved for public release; distribution unlimited.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave Blank*)

2. REPORT DATE
June 27, 1994

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
Development of a Dosimeter System for Unsymmetrical Dimethylhydrazine, Monomethylhydrazine and Hydrazine

5. FUNDING NUMBERS

6. AUTHOR(S)
Karen P. Brenner* and Susan L. Rose-Pehrsson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Research Laboratory
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER
NRL/MR/6110--94-7492

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Head Quarters Space and Missile System Center
P.O. Box 92960
Los Angeles AFB, CA 90009-2960

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
*Geo-Centers, Inc., Fort Washington, MD 20744

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)
A dosimeter for real-time, colorimetric detection of current and proposed threshold limit value (TLV) levels of hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) in air has been developed. The dosimeter consists of a replaceable dosimeter card and a reusable, polypropylene badge housing containing a clear, UV adsorbent shield. The replaceable dosimeter card has two reaction sites, each containing one of two chemistries on a paper substrate. One chemistry uses 2,4-dinitrobenzaldehyde which is an excellent derivatization agent for UDMH, though less effective for hydrazine and MMH. Through a condensation reaction, 2,4-dinitrobenzaldehyde reacts with UDMH to form a colored product that absorbs in the visible region. The hydrazone formed in the reaction is yellow to golden yellow. The intensity of the color is proportional to the dose. When coated on porous filter paper and exposed passively to UDMH, the detection limit is <20 ppb-hrs. Actively drawing UDMH vapors through the paper gives a detection limit of <50 ppb-L. The second reaction utilized in the dosimeter system involves 3-methoxy-4-hydroxbenzaldehyde (vanillin) for the detection of hydrazine and MMH (U.S. patent 4,900,681). In the reaction between vanillin and hydrazine or MMH, a yellow hydrazone is formed. When coated on porous filter paper and exposed to MMH or hydrazine, the detection limit is 7 ppb-hours. Neither chemistry is hindered by a sensitivity to relative humidity changes. Badges remain sensitive to hydrazines vapors for at least one year when stored in a freezer. Interferences with the chemistries are limited to tobacco smoke and sunlight for the vanillin and 2,4-dinitrobenzaldehyde chemistries, respectively. The incorporation of a polyester sheet impregnated with UV inhibitors, controls the sunlight effect. A field test of the passive system indicated that it can be used for two consecutive days in the sunlight. For indoor applications, the passive badges can be used for at least one week. There were no false positives or negatives for any sites tested.

14. SUBJECT TERMS
UDMH   Hydrazine   Dosimetry
MMH   Vapor detection

15. NUMBER OF PAGES
36

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18
298-102

CONTENTS

DEVELOPMENT OF A DOSIMETER SYSTEM FOR UNSYMMETRICAL DIMETHYLHYDRAZINE, MONOMETHYLHYDRAZINE AND HYDRAZINE

INTRODUCTION

The three hydrazines currently used by the Department of Defense as hypergolic fuels are hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH). Hydrazines are used as propellants in space launch vehicles, satellites and aircraft emergency power units. Because of this widespread use, concern has developed over the toxicological properties of the compounds.

The American Conference of Governmental Industrial Hygienists (ACGIH) has categorized the hydrazines as suspected human carcinogens and has recommended threshold limit values (TLV) for hydrazine, MMH, and UDMH of 100, 200 and 500 parts-per-billion (ppb), respectively.[1] Potentially this level will be lowered to 10 ppb for all three hydrazines.[2] To minimize the risk of exposure, monitoring of employees, who come into contact with hydrazines, and of the associated work environments should be conducted to insure that the presence of hydrazines remains below hazardous levels. The Department of Defense and NASA require air monitoring for hydrazines in areas where they are handled and/or stored.

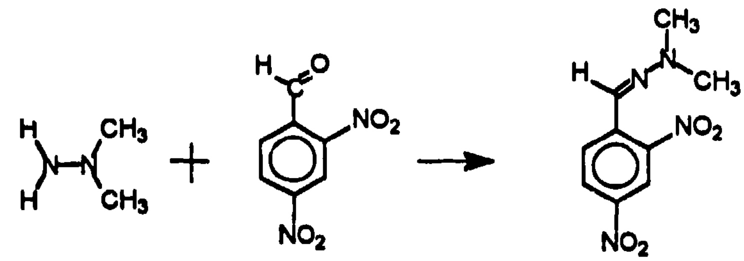
A real-time dosimeter using vanillin to detect hydrazine and MMH was developed and patented at the Naval Research Laboratory (NRL).[3] The badge has been fully characterized through extensive laboratory evaluation and field testing.[4] Because vanillin does not detect UDMH and a similar dosimeter for reliable, real-time detection of UDMH would be useful, a new method was developed at NRL and Geo-Centers, Inc. With the joint efforts of NRL and Geo-Centers, Inc. and GMD Systems, Inc., a passive dosimetry system which detects all three hydrazines in real-time and an active dosimeter for the detection of UDMH were designed and evaluated.

THEORY

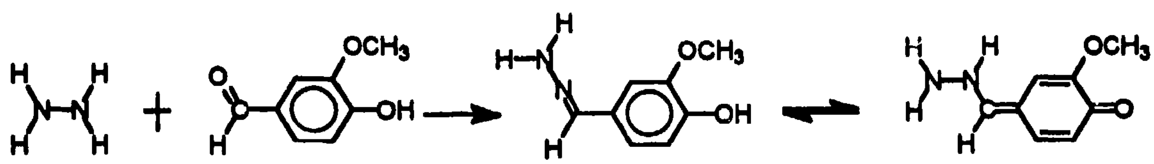
The extreme reactivity of the hydrazines is responsible for a variety of technical problems encountered in performing ambient air monitoring. One approach that utilizes this reactivity is derivatization of the hydrazine to a species that is easier to analyze. One method is based on the condensation of a hydrazine and an aldehyde, resulting in a product known as a hydrazone. In the case of unsubstituted hydrazine, two moles of aldehyde can react with one mole of hydrazine to form an azine. The mechanism involves the nucleophilic addition of the nitrogen base, followed by the elimination of water. This reaction is acid catalyzed by protonation of the carbonyl. A well-known ASTM method uses para-N,N-dimethylaminobenzaldehyde (PDAB) in a condensation reaction.[5] Although PDAB is a good derivatization agent for hydrazine and MMH, it is subject to a host of interference effects as a passive dosimeter.

Manuscript approved May 12, 1994.

The two chemistries used in this dosimeter are 2,4-dinitrobenzaldehyde and vanillin. Both aldehydes react with hydrazines through condensation reactions to form yellow colored products which absorb in the visible region. Figures 1a and b show the reactions between UDMH and 2,4-dinitrobenzaldehyde and between hydrazine and vanillin, respectively. While vanillin reacts rapidly with MMH and hydrazine, it does not react sufficiently with UDMH for use as a real-time dosimeter. The reaction between vanillin and MMH produces a hydrazone; with hydrazine, both the azine and hydrazone products are observed. Acidification is required in the 2,4-dinitrobenzaldehyde reaction with UDMH to form a yellow colored hydrazone. Phosphoric acid was found to be the most suitable choice for a paper substrate based dosimeter.



(a)



(b)

Figure 1. Condensation reactions between a) UDMH and 2,4-dinitrobenzaldehyde and b) hydrazine and vanillin.

EXPERIMENTAL

EXPERIMENTAL SET-UP

In the laboratory experiments that contributed to the characterization of the final passive dosimeter system and active sampler, the following system was utilized for generation of hydrazine, MMH and UDMH vapors. This dynamic system supplied hydrazine, MMH and UDMH concentrations ranging between 0.005 to several parts-per-million (ppm). A diffusion tube containing the propellant grade liquid hydrazine of choice was housed in a constant temperature bath and continually purged with 100 mL/min of dry nitrogen to provide the

vapors. All three hydrazines were obtained from Olin Chemicals. The desired concentration was obtained by adjusting the temperature of the bath, the size of the diffusion capillary and/or the amount of dilution air. Conditioned house-compressed air was used as the diluent. The conditioning procedure consisted of passing the house air through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular sieve scrubber and finally through a canister containing potassium permanganate coated alumina (Purafil) and charcoal. The cleaned air was humidified using a stainless steel gas washer (bubbler) containing distilled, deionized water. Control of the relative humidity was achieved by varying both the gas washer head pressure and the ratio of the humidified to dry air. The moisture content of the air was measured by a Hygrodynamics hygrometer (Silver Spring, MD). The dilution air was monitored with calibrated mass flow controllers capable of providing up to 10 L/min (Matheson Gas Products, East Rutherford, NJ).

Passive and active exposures were conducted. Passive dosimeters were designed for use as personnel and area detectors which could be used for at least one 8 hour workday. The active dosimeters were designed for one-time use to yield rapid results, typically in a 5 minute sampling period at a sampling rate of 1 to 2 L/min. In evaluating the badges, the following laboratory design was utilized. The laboratory experiments were carried out in a cylindrical glass chamber with hemispherical ends. Teflon baffles placed at each end of the chamber induced laminar flow. The exhaust end was removable to allow insertion of the dosimeters. Evaluation of passive badges was conducted by inserting badges into the chamber in a side-by-side, staggered fashion. For active exposures, vapors were drawn through the badge at approximately 1 L/min using a personal pump. The face velocity in the chamber for early evaluations was approximately 2.6 ft/min. It was increased to 5.2 ft/min for later exposures.

The coulometric titration procedure used to verify the concentrations of the dynamic test environment has been characterized at NRL.[6] It involves the electrochemical generation of bromine from potassium bromide and the subsequent reaction of bromine with hydrazine, MMH or UDMH in solution. The reaction relies on amperometric endpoint detection.

CHEMICAL SURVEY

Vanillin had already been identified and characterized for detection of hydrazine and MMH. The next step was to identify a compound which would form a colored product upon reaction with UDMH in real-time. A number of compounds were investigated for their reactivity with UDMH in active and passive systems. Whatman filter paper disks (#42) were coated with the compounds in solution and exposed to UDMH vapor. Table I indicates the chemistries examined.

Table I. Chemical Survey

Compound	Color Development with UDMH	Comments
salicylaldehyde	yellow	poor stain stability
1,4-naphthoquinone	wine	poor storage stability low sensitivity to UDMH
2-hydroxy-1,4-naphthoquinone	orange	low sensitivity to UDMH sensitivity to light
phosphomolybdic acid	blue green	low sensitivity to UDMH
2-nitrobenzaldehyde	golden yellow	sensitivity to light
3-nitrobenzaldehyde	yellow	fair sensitivity to UDMH
4-nitrobenzaldehyde	yellow	good sensitivity to UDMH
2,4-dinitrobenzaldehyde	golden yellow	excellent sensitivity to UDMH

OPTIMIZATION OF BADGE SYSTEM

Based upon the promising results of 2,4-dinitrobenzaldehyde, further work was focused on this chemical. Dosimeters were prepared by soaking filter paper disks in a 0.5% solution of 2,4-dinitrobenzaldehyde dissolved in acetone and acidified with phosphoric acid. The hand coated filter papers were then allowed to air dry. The coated disks were exposed both actively and passively to UDMH vapors using the vapor generation system described previously.

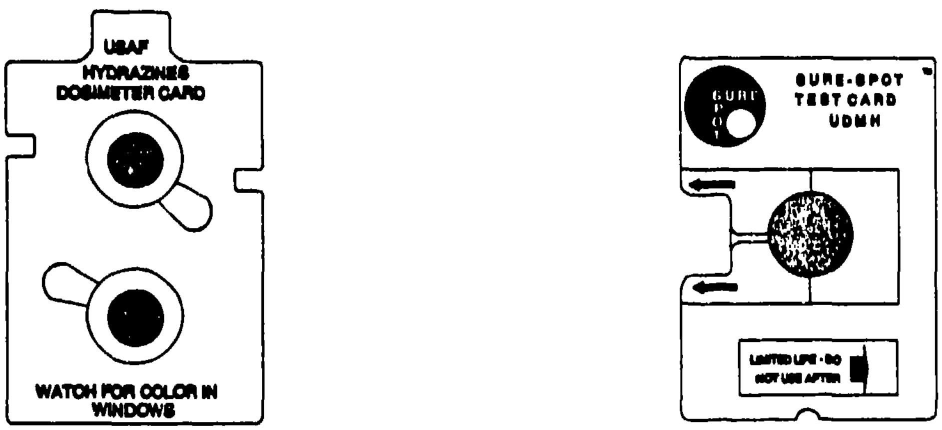
The color development of the badges was evaluated on a color wheel prepared by GMD Systems, Inc. (Hendersonville, PA) for the passive v inillin colorimetric dosimeters. The wheel contains 5 shades of yellow of increasing intens y which correlate to MMH and hydrazine dose. 2,4-Dinitrobenzaldehyde disks were examined for dose-response, relative humidity effects, potential interference effects (tobacco smoke, nitrogen dioxide (NO_2) and ammonia (NH_3)) and accelerated shelf life tests. To eliminate an interference effect caused by exposure to sunlight, chemical ultraviolet absorbers and antioxidants/inhibitors were investigated with minimal success. LLumar, a transparent polyester sheet impregnated with UV absorbers was obtained.[7] It effectively blocks UV interference; however, it is not permeable to UDMH vapors.

The optimal performance of 2,4-dinitrobenzaldehyde was investigated with various substrates, aldehyde concentrations and pH levels. Tests were performed to determine the substrate which afforded the most stable and linear color development when coated with 2,4-dinitrobenzaldehyde and exposed to UDMH. Because it was previously determined that the 2,4-dinitrobenzaldehyde chemistry required acidification for real-time response with UDMH,

the substrates were coated with 2,4-dinitrobenzaldehyde solutions acidified to pH values of 2 to 5. The solutions were acidified with either hydrochloric acid (HCl) or phosphoric acid. Optimal badge design was investigated at this stage.

EXTENSIVE LABORATORY EVALUATION OF THE BADGE SYSTEM

After the effectiveness of the LLumar as a UV shield was determined and the optimum benzaldehyde concentration, pH and substrate were selected, an extensive laboratory evaluation was undertaken. Desired badge parameters were supplied to GMD Systems where the paper tape substrate was machine coated and the cardboard insert cards containing the coated substrate were assembled. The cards measuring 6.8 cm x 4.5 cm x 0.05 cm featured two reaction sites, both encircled by a clear plastic contrast ring to facilitate visual determination of color development. The paper substrate in the top site of the passive card was machine coated with a 2% 2,4-dinitrobenzaldehyde/2% acid solution, while the bottom site of the badge contained a paper substrate coated with a 2% vanillin/2% acid solution. GMD supplied active UDMH cards using a design similar to their commercially available active cards called Sure-Spots. The Sure-Spot cards contained one reaction site coated with the 2,4-dinitrobenzaldehyde formula. The processed badges were sealed in plastic/foil wrappers by the manufacturer. Figure 2 shows the passive and active card designs.

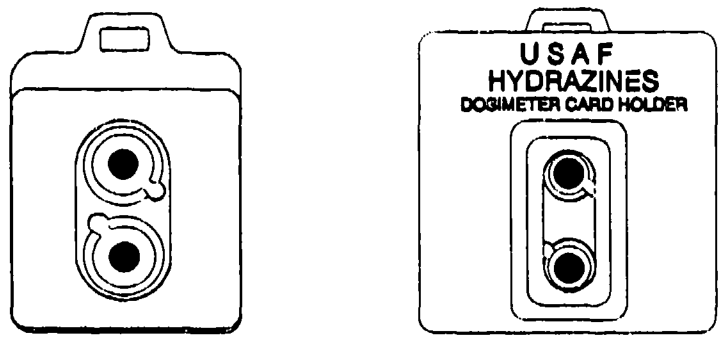


(a) (b)

Figure 2. Hydrazine dosimeter cards for a) passive and b) active sampling.

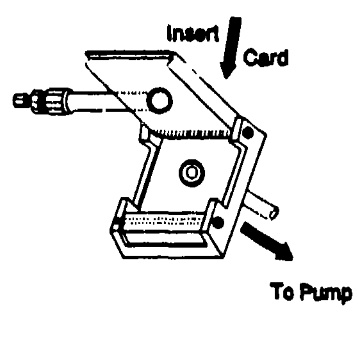
The passive badge housing designed for this evaluation was molded from black polypropylene. A molded face plate measuring 5.1 cm x 7.0 cm secured a clear, plastic UV shield (LLumar) at a height of 0.6 cm above the front of the badge to allow gas to diffuse to the reaction sites. The front of the badge was designed with the LLumar window measuring 2.2 cm x 4.7 cm through which the reaction sites of the hydrazine cards could be viewed. The back of the badge was hinged to the front portion, allowing the hydrazine card to be

slipped into the housing and held securely in place. Based on sunlight exposures conducted during the laboratory evaluation, this housing was modified to include a larger face plate (7.5 cm x 8.3 cm), a smaller window (1.4 cm x 3.8 cm) and increased LLumar thickness (21 mil) to alleviate damaging UV effects. Figure 3 shows the passive badge housing used for the laboratory evaluation as well as the modified housing used in a field test conducted at Cape Canaveral. GMD Systems and NASA provided NRL with sample holders for the active cards (see Figure 4).



(a) (b)

Figure 3. Schematic of the a) original and b) modified passive badge housing.



(a) (b)

Figure 4. Active samplers for use with Sure-Spot cards: a) GMD Systems design and b) NASA design.

The GMD designed active holder was made of metal equipped with a teflon tubing insert for introducing the test gas. The rectangular active sample holder designed by NASA to hold the Sure-Spot cards was made of clear plexiglass (6 x 8 x 1.5 cm), allowing the user to visually note any color change on the insert card.

Concentrations of UDMH from 10 to 500 ppb were generated for both passive and active badge exposures. Tests were conducted in the glass exposure chamber described previously. By varying the exposure time, badge response to doses of UDMH ranging from approximately 20 to 2000 ppb-hours was examined. The relative humidity was maintained at approximately 30 to 40% for the dose response exposures. In addition, badges were examined for relative humidity effects, potential interference effects (tobacco smoke, NO_2, NH_3, hydrazine, MMH, heat, cold and sunlight), response to Aerozine-50, accelerated shelf life, storage stability and field interferences.

All passive badges were exposed in groups of four in order to provide replicate samples. In many dose response tests, eight passive badges were exposed in two identical tests to provide additional replicates. Aging tests consisted of two aged badges and two fresh badges for both the passive and active tests. Four badges were used in active exposures to determine dose response and relative humidity effects. For interference tests, two active badges were exposed to UDMH before the interferences and two were exposed to UDMH after the interferences. Badges were exposed to vapors generated from a 1:1 (by weight) mixture of hydrazine and UDMH to examine the badge response to Aerozine-50. For accelerated shelf-life tests, sealed badges were placed in an oven maintained at a temperature of 40°C for approximately 1 week. After the badges were "aged" at the increased temperature, they were exposed to various doses of UDMH alongside badges stored at room temperature. In extensive sunlight exposures at Kennedy Space Center (KSC) and NRL, badges were exposed for multiple days to determine the serviceable life of the badge in outdoor use.

Color development on the badges was determined with the color wheel and a densitometer.[8] The densitometer measured the reflective color of the badge surface.

For the storage stability study, 25 passive and 25 active badges were placed in the freezer. An additional 25 passive and 25 active badges were held in the laboratory at room temperature. The badges were held in their respective storage conditions for 4 months prior to the onset of exposures for storage stability. Approximately once per month, two passive insert cards were removed from the freezer and exposed alongside two room temperature insert cards in the chamber described previously. The cards were placed in the molded housing before being inserted into the chamber. With the exception of two tests, badges were exposed to approximately 30 ppb of UDMH. The relative humidity of the atmosphere was maintained at 22% to 32% RH.

FIELD TEST

Locations for field testing at Cape Canaveral were chosen based upon their potential for exposure to UDMH and for providing information on potential interferences. Test locations selected were divided into exposure categories, Unlikely Exposure and Highly Probable Exposure. All site tests were performed for one work week (Monday through Friday) except

the Highly Probable Exposure propellant and cart loads. Table II gives the sites chosen for the field test. At each test site, personnel and area monitoring was performed.

Table II
Field Test Locations at Cape Canaveral

Test Site	Vapor for Potential Exposure
Unlikely Exposure	
Complex 17 Tower	Aerozine-50, liquid O_2, nitrogen tetroxide (not in use)
FSA #1	hydrazine, MMH, nitrogen tetroxide, JP-5, RP-1, citric acid (not in use)
Air Force Chemistry Laboratory	typical laboratory chemicals: acids, bases, solvents
Paint Shop	enamels, vinyl-based inks, mineral spirits, MEK, polyurethane paints, isocyanate paints, wood lacquer, paint thinner, xylene, naphtha
Highly Probable Exposure	
Complex 17 - Propellant Load (SCAPE)	Aerozine 50, liquid O_2, nitrogen tetroxide
Air Force Chemistry Laboratory	hydrazine, MMH, UDMH, typical laboratory chemicals
Complex 40	Aerozine-50, hydrazine
FSA #1 - Cart Load (SCAPE)	Aerozine-50

Reference methods incorporated into the field test were citric acid samplers and liquid impingers. The citric acid sampler was designed and evaluated at NRL.[9,10] The sampler is molded from black, low density polyethylene and holds a replaceable paper substrate coated with a citric acid solution. The sampler can hold a substrate on either side. A cap containing 144 holes allows for diffusion of vapors into the badge. Because the citric acid sampler is not a real-time dosimeter, the substrate must be analyzed in the laboratory. Two methods were used for analyzing the citric acid samplers. The first was the coulometric analysis method described previously.[8] The second was a NIOSH approved colorimetric method using phosphomolybdic acid.[11]

Liquid impingers were also used as a reference method for the field test. The impingers were analyzed with the NIOSH approved colorimetric method using phosphomolybdic acid.[11] The impingers used 0.1 M hydrochloric acid (HCl) as the collection medium for trapping UDMH. The impingers were attached to a personal pump drawing sample through the collection medium at 200 mL/min.

Personnel monitoring was handled in the following fashion. After the test location was chosen, two workers at the site were badged each day of the 5 day period. Each worker wore two passive colorimetric badges and two citric acid samplers. These badges were dispensed to the workers each morning and collected every evening. Two additional workers at each site wore the same badges (2 passive colorimetric, 2 citric acid) for two and three days in a row. They received their badges on Monday morning and wore them through Tuesday evening. These same workers received fresh badges on Wednesday morning and wore them through Friday evening. The colorimetric badges worn Monday through Tuesday and those worn Wednesday through Friday were measured every evening with the color wheel and the densitometer and replaced in the holder the following day for continued use. In general, citric acid samplers were stored in the refrigerator for up to 1 week and analyzed in one batch.

Laboratory badge blanks were incorporated into the test plan. A passive colorimetric badge blank remained in the laboratory for each day of the site test. The collection schedule mirrored that of the personnel badges. For example, a badge card was inserted into a housing and placed in the laboratory on Monday morning. The badge remained in the lab until evening when it was measured alongside the "exposed" badges . In addition, a blank badge mirroring the 2 day and 3 day "exposed" badges was prepared each week of the field test. The blanks of the citric acid samplers were prepared by placing an additional coated substrate in the back of the sampler worn by personnel. The badge blank side was assembled similarly to the exposed side of the badge, except that a cap was placed over the diffusor. This provided a blank for every badge worn. At least two blanks were analyzed for each batch of samples analyzed.

Passive colorimetric badges and citric acid samplers, mounted on a board together with colorimetric active badges and impingers, were used for area sampling. Two boards were used at each test site. Six passive colorimetric badge housings and two field blank housings were permanently affixed to the two boards. The blank badges contained an insert card and were taped on all sides to prevent vapors from entering the housing. On Monday morning, inserts were placed in each of the six holders. Three exposed cards and one blank were removed each evening and the color development measured. The remaining three exposed cards and a blank were left on the board from Monday to Tuesday evening when they were removed and measured. On Wednesday morning, four fresh inserts were placed in the housings (this includes the blank) and left on the boards until Friday evening when they were measured.

Two citric acid samplers were placed on both boards each morning and collected for analysis each evening. In addition, two more citric acid samplers (including blanks) were placed on the boards on Monday mornings and collected on Friday evening. One liquid impinger was placed each morning at both boards. The impingers sampled for the entire exposure time of the badges each day. The impingers were collected each evening and stored in the refrigerator for later analysis. For each day of testing, two active Sure-Spot badges at each board were sampled for 5 minutes apiece at a sampling rate of 2 L/min.

For analysis of the citrate samplers, one of the two daily personnel samplers and one of the two daily area samplers from each board were analyzed coulometrically. If a detectable amount of analyte was found on any of these badges, the second badge of the pair was

analyzed by either coulometry or the NIOSH method depending upon the amount of UDMH found on the previously analyzed badge. This was also the procedure for the twice weekly personnel samplers and the weekly area samplers. To decrease the labor intensity of the task, the samplers were gathered at the appointed times, capped and stored in the refrigerator until analyzed.

Badges that were used in the field test were sent to NRL for exposure to UDMH vapors in the glass chamber. This was done to insure that field exposure had not caused a decrease in the sensitivity of the badge to UDMH vapors. To mimick the field exposure sampling conditions of the active badges, UDMH vapors were sampled at a rate of 2 L/min.

The tasks for conducting the field test were divided between the EG&G industrial hygienist located at KSC, the Air Force analytical lab located at Cape Canaveral and personnel at NRL. The tasks for those involved were as follows:

Industrial Hygienist: 1) maintained all data sheets including a facility data sheet, sample data sheet and activity log; 2) measured the colorimetric badges using the color wheel unit and the densitometer and recorded information on the sample data sheets; 3) stored passive colorimetric badge housings and impingers; 4) distributed all badges and impingers to sites prior to test and collected all badges and impingers after test; 5) sent data sheets and exposed colorimetric badges to NRL.

Analytical Laboratory: 1) stored citric acid samplers prior to dissemination to sites; 2) cleaned and assembled the citric acid samplers prior to each site test; 3) prepared all solutions for the analytical methods except the citric acid solution; 4) stored all exposed citric acid samplers and impingers received from EG&G in the refrigerator until analysis; 5) analyzed the citric acid samplers and liquid impingers by the appropriate methods.

NRL: 1) trained the technicians at the analytical laboratory to use the coulometric method and the NIOSH PMA method; 2) instructed the industrial hygienist on the use of the color wheel unit and the densitometer; 3) provided the analytical lab with chemicals needed to analyze citric acid samplers and impingers; 4) prepared and shipped citric acid sampler substrates to the analytical lab; 5) supervised the initial stage of the field test to insure that the process ran smoothly; 6) catalogued all data sheets sent from the industrial hygienist; 7) verified badge sensitivity of used colorimetric badges (active and passive) after field exposure; 8) analyzed data and wrote final report.

RESULTS

INITIAL BENZALDEHYDE EVALUATION RESULTS

Figure 5 shows the dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde when used as active samplers. The first visual indication of color for 2,4-dinitrobenzaldehyde was at 130 ppb-L. This means that a vapor concentration of 10 ppb could be detected in as little as 13 minutes when sampled at 1 L/min. If the sampling rate were increased, the response time would decrease. Saturation occurred at approximately 4000 ppb-L with a color index of 5. The initial results for 4-nitrobenzaldehyde indicated that the compound was less sensitive to UDMH than the dinitro- compound. A dose of 500 ppb-L was needed to produce the first visual indication of color and a dose of almost 74,000 ppb-L was required to give a color index of 3.5 on the color wheel.

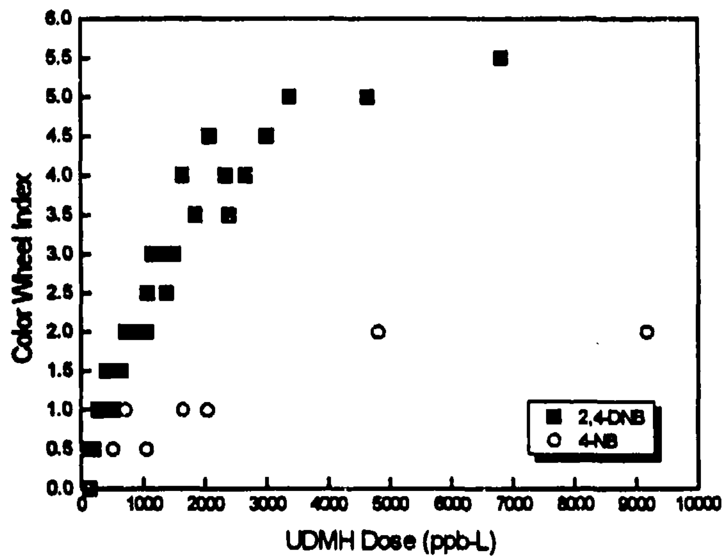


Figure 5. Dose response of active samplers hand coated with 2,4-dinitrobenzaldhyde or 4-nitrobenzaldehyde.

Figure 6 shows the dose response curves for 2,4-dinitrobenzaldehyde and 4-nitrobenzaldehyde used as passive dosimeters. All of the exposures were made at approximately 10 ppb of UDMH. There was a visual first indication of color within 14 ppb-hours with 2,4-dinitrobenzaldehyde. The average scatter in the data points is limited to approximately ±0.5 on the color index scale. There was insufficient data to make a determination of saturation dose. The responses observed one hour later were similar, indicating satisfactory color stability. A 10% to 20% reduction was observed for higher doses when evaluated 24 hours after exposure. 4-Nitrobenzaldehyde performed less satisfactorily

as shown on the graph. A color index of <1 was reached within 77 ppb-hours. The color intensity of the badge increased slowly from first indication to a color index of 3.5 within 1250 ppb-hours. At this point in the investigation, it was decided to concentrate further efforts on 2,4-dinitrobenzaldehyde.

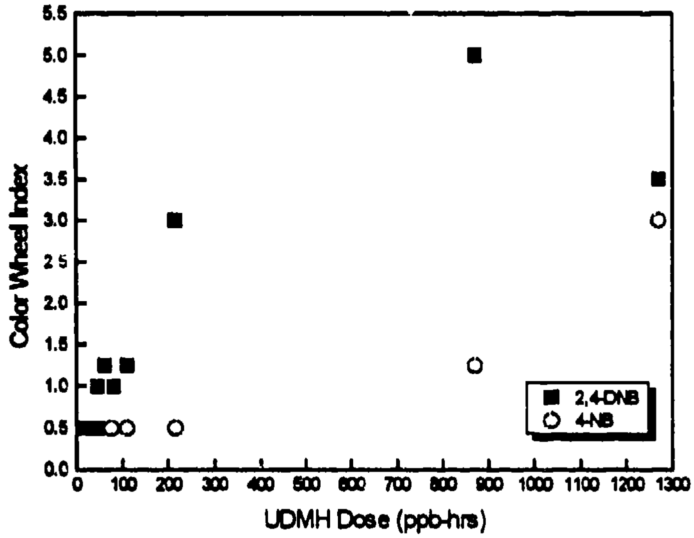


Figure 6. Dose response of passive badges hand coated with 2,4-dinitrobenzaldhyde or 4-nitrobenzaldehyde.

Neither variations in relative humidity nor artificial aging had a significant effect on color development with 2,4-dinitrobenzaldehyde. Badges that were "aged" in the oven at 40°C for one week did not discolor and performed comparably to badges stored at room temperature. Interference tests performed on the coated disks indicated that NH_3 was not an interferent to the 2,4-dinitrobenzaldehyde chemistry. Badges exposed to NO_2 after UDMH exposure showed a slight bleaching of the color. Passive exposures to tobacco smoke showed normal color development with subsequent UDMH exposure. Active exposure to tobacco smoke indicated slightly enhanced color development with subsequent exposure to UDMH.

The 2,4-dinitrobenzaldehyde exhibited a sensitivity to sunlight which hinders the reaction with UDMH. In an effort to eliminate this effect, disks were coated with mixtures of various UV absorbers or inhibitors and 2,4-dinitrobenzaldehyde. These disk were then exposed to sunlight or UV lamp light with a wavelength of 254 nm. None of the substances tested effectively eliminated the UV light interference effects. LLumar was examined and found to effectively block UV interference on the 2,4-dinitrobenzaldehyde coated disks. Coated disks covered with LLumar and exposed for up to 3.5 hours of sunlight showed no color development. UV-visible spectra show that LLumar absorbs in the same region as the 2,4-dinitrobenzaldehyde.

For badge optimization, the combination of either Whatman Chroma 1 or GMD SS-410 substrates coated with a 2,4-dinitrobenzaldehyde solution acidified to a pH of 5 provided the best results. Phosphoric acid was chosen as it had performed well in previous tests and possesses favorable acid strength and non-volatility required for dosimetry applications. It was also decided to use a 0.5% 2,4-dinitrobenzaldehyde solution as there was no significant difference in color development between concentrations of 0.5 and 1.0%.

EXTENSIVE LABORATORY EVALUATION OF THE BADGE SYSTEM

Dose Response

The passive badges were exposed to doses ranging from 20 to 2000 ppb-hours of UDMH. Figures 7a and b show the dose response of the 2,4-dinitrobenzaldehyde site on the passive badges immediately after exposure. Figure 7a shows the median color at each dose category and the 95% confidence intervals as measured with the color wheel. Figure 7b shows the average color and the 95% confidence intervals as measured with the densitometer. Color development reached a saturation within 1800 ppb-hrs with a color wheel index of 5 and a densitometer value of 65. There was no significant change in the color on the badges within one hour after exposure. Twenty-four hours after exposure, the badge color showed an average decrease of 20%, corresponding to a decrease of 3.50 units on the densitometer. This decrease fell within the normal deviation in color development and did not constitute a significant decrease. Using the color wheel, a decrease of 15% was noted within 24 hours after exposure.

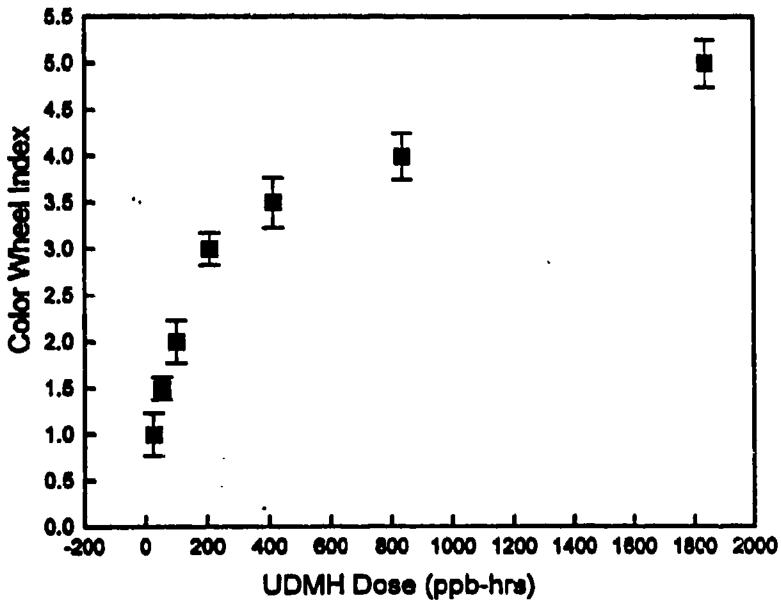


Figure 7a. Dose response, using the color wheel, of passive badges machine coated with 2,4-dinitrobenzaldehyde.

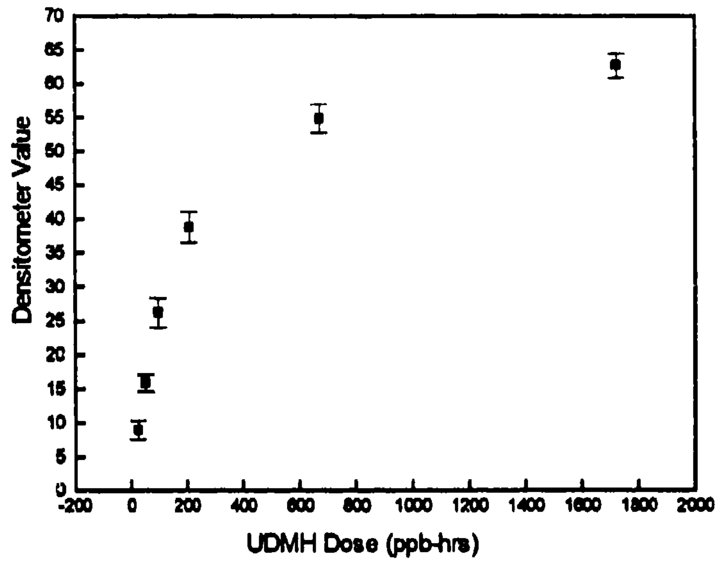


Figure 7b. Dose response, using the densitometer, of passive badges machine coated with 2,4-dinitrobenzaldehyde.

Although the data are not shown graphically categorized by concentration, the response of the badge has been determined to be dose dependent, not concentration dependent. Table III gives the densitometer and color wheel values typical of dose ranges for passive exposures.

Table III
Typical Measurement Values at Specified Dose Ranges (Passive)

UDMH Dose (ppb-hrs)	Densitometer Value	Color Wheel Value
20 - 30	8.97 ± 2.60	1.0 ± 0.5
35 - 70	15.92 ± 4.94	1.5 ± 0.5
75 - 140	25.85 ± 5.35	2.0 ± 0.5
145 - 275	40.15 ± 6.59	3.0 ± 0.5
350 - 940	54.86 ± 6.53	3.5 ± 0.5
1140 - 1450	60.96 ± 4.09	4.0 ± 0.5
1700 - 2135	63.61 ± 3.56	5.0 ± 0.5

In general, the vanillin site on the passive badges did not develop color upon exposure to UDMH. At doses greater than 1500 ppb-hrs of UDMH, a very slight yellow color was apparent immediately after exposure. In some tests, slight color was visible within one hour after exposure. At this level of visual color, measurement with the color wheel is very subjective and cannot be expected from a person unfamiliar with the badges. Any color that developed after exposure was attributed to the slow reaction occurring between UDMH and vanillin. The reaction is slow enough that color does not develop during the tests, but within one hour after removal from the chamber, some color is evident.

The active Sure-Spot badges coated with 2,4-dinitrobenzaldehyde were exposed to doses of UDMH ranging from 50 to 8500 ppb-L by varying concentration and exposure time. Figures 8a and b show the dose response plots for active exposures. The median color at each dose category and the 95% confidence intervals as measured with the color wheel are shown in Figure 8a. Figure 8b shows the average color and 95% confidence intervals at a given dose as measured with the densitometer. Although the saturation dose could not be determined, the dosimeters did not attain a color more intense than a 4 on the color wheel within the range tested. As with the passive badge, the response of the active badge proved to be dose dependent, not concentration dependent. Table IV gives the densitometer and color wheel values typical of dose categories for active exposures.

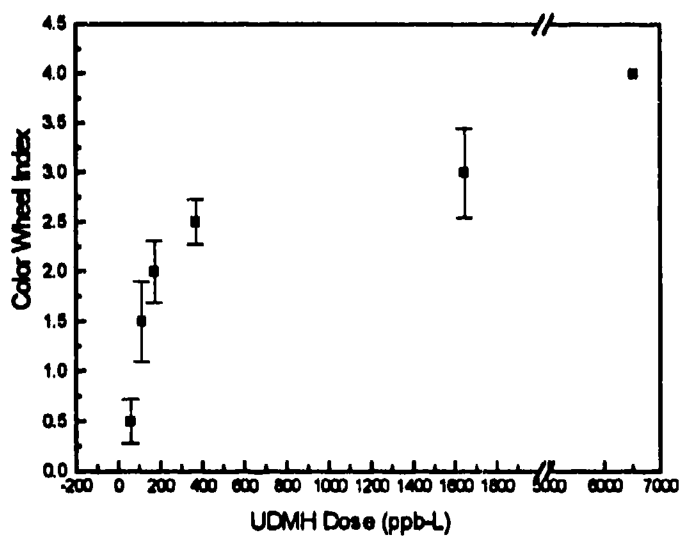


Figure 8a. Dose response, using the color wheel, of active badges machine coated with 2,4-dinitrobenzaldehyde.

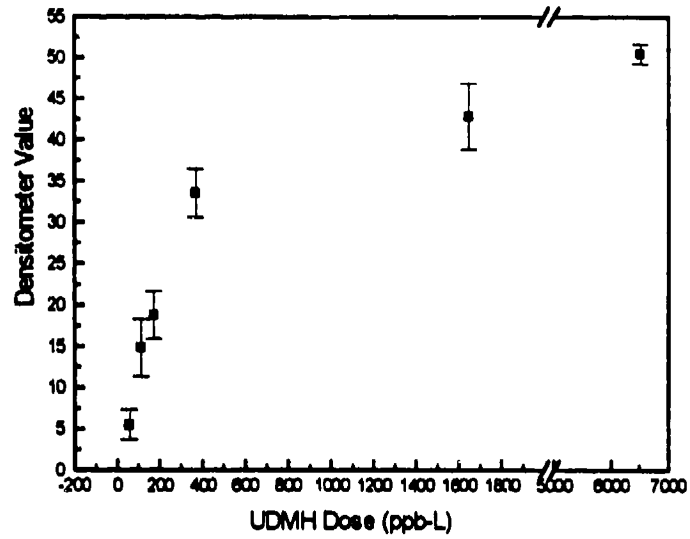


Figure 8b. Dose response, using the densitometer, of active badges machine coated with 2,4-dinitrobenzaldehyde.

Table IV
Typical Measurement Values at Specified Dose Ranges (Active)

UDMH Dose (ppb-L)	Densitometer Value	Color Wheel Value
50 - 60	5.52 ± 2.01	0.5 ± 0.0
100 - 120	14.87 ± 4.28	1.5 ± 0.5
145 -190	18.66 ± 5.42	2.0 ± 0.5
285 - 540	33.57 ± 6.29	2.5 ± 0.5
560-3740	42.87 ± 9.08	3.0 ± 0.5
4650 -8475	50.47 ± 1.59	4.0 ± 0.5

Relative Humidity Effects

Passive badges were exposed to UDMH humidified to <10%, 40% and 90% RH. Doses of UDMH ranged from 45 to 2100 ppb-hrs. Figure 9 shows the dose response of the passive badges at several doses and low, mid and high humidities. With the exception of a

low response to an exposure at approximately 1800 ppb-hrs and < 10% RH, there appeared to be no significant effect of relative humidity extremes on badge response to UDMH. Active badges were exposed to doses of 150, 550 and 900 ppb-L of UDMH at low, mid and high humidities (Figure 10). At the lower doses, exposure to 90% RH appeared to hinder color development on the active badges. This was not observed for the exposure at 900 ppb-L, however.

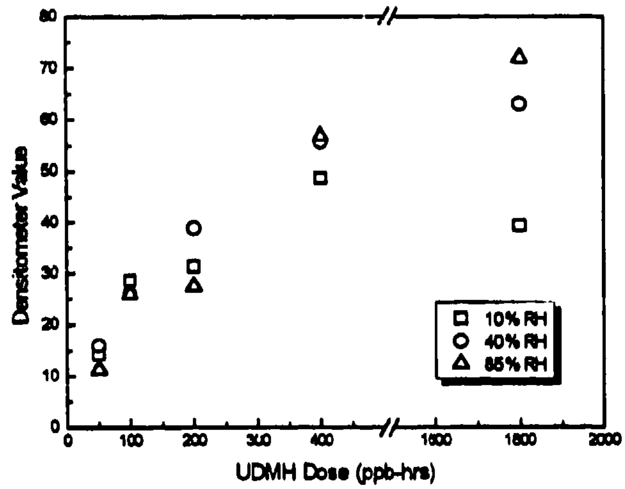


Figure 9. Passive badge response to hydrazine at low, medium and high relative humidities.

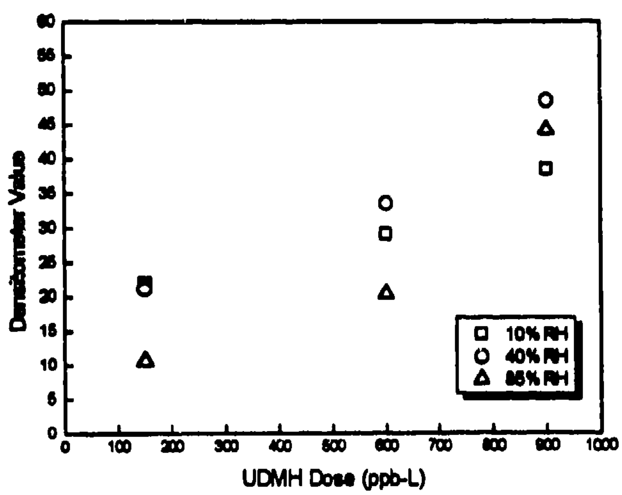


Figure 10. Active badge response to hydrazine at low, medium and high humidities.

Interference Effects

Four passive badges and two active badges were exposed before and after exposure to potential interferences. The passive badges were exposed to UDMH and the interferent for four hours each. The active badges were exposed to UDMH and the interferences for 15 to 20 minutes at 1 L/min. Interferences tested in the laboratory included heat (40°C), cold (-15°C), NO_2, NH_3, tobacco smoke, MMH and hydrazine. Tables Va and Vb show the effects of the interferences that affected the 2,4-dinitrobenzaldehyde site on the passive badges in some manner. The only interference vapor which reacted with the 2,4-dinitrobenzaldehyde chemistry to form a colored compound was MMH. This was expected as it was shown in early tests that the 2,4-dinitrobenzaldehyde chemistry is slightly sensitive to MMH vapors. However, exposure to MMH does not hinder normal color development when subsequently exposed to UDMH. As shown in Table Vb, there was no color development in the presence of heat alone; however, with subsequent exposure to UDMH, the color development was hindered. This effect can be explained by the volatilization of 2,4-dinitrobenzaldehyde from the substrate when heated. Therefore, when the badge is subsequently exposed to UDMH, there is less reagent on the substrate to react with UDMH allowing less color development. In addition, the heat may have caused decomposition of the 2,4-dinitrobenzaldehyde.

Table Va
Monomethylhydrazine Effects on Passive Badge (2,4-Dinitrobenzaldehyde Site)

Test Vapor	Dose (ppb-hrs)	Densitometer Value	Color Wheel Value
UDMH	70	23.91 ± 5.66	2.0 ± 0.5
MMH	168	27.99 ± 5.79	2.5 ± 0.5
MMH	168	7.42 ± 3.80	0.5 ± 0.5
UDMH	70	28.22 ± 7.62	2.5 ± 0.5

Table Vb
Heat Effects on Passive Badge (2,4-Dinitrobenzaldehyde Site)

Test Vapor or Interferent	Dose (ppb-hrs)	Densitometer Value	Color Wheel Value
UDMH	70	25.05 ± 4.45	no data
heat (40°C)	NA	22.72 ± 4.71	2.0 ± 0.5
heat (40°C)	NA	0.08 ± 0.09	no data
UDMH	70	11.66 ± 2.65	1.0 ± 0.5

In the interference evaluation of the 2,4-dinitrobenzaldehyde active badges, it was typical for the badge color to increase when exposed to an interferent subsequent to UDMH exposure. Control badges were exposed to compare with the interference vapor data and determine the significance of the increase. The control exposures were made by sampling UDMH vapor and then either drawing room air through the badge at 1 L/min, or allowing the badge to passively sample room air for 30 minutes. Table VI shows that the controls exhibited similar behavior both for active and passive room air exposure after UDMH exposure. The data show that densitometer readings should be taken immediately after exposure. This is the normal behavior of the badge after exposure to UDMH and should be accounted for when sampling in the field.

Table VI
Control Badges

Test Vapor	Dose (ppb-L)	Chroma Value
UDMH	498	28.46
room air	32 L	47.38
UDMH	462	26.47
passive room air	30 min	49.35

Aerozine-50 Response

In the Aerozine-50 response studies, air samples were used in which hydrazine and UDMH vapors were present in high ppb concentrations (approximately 900 ppb). Since the coulometric method cannot distinguish between the hydrazines, giving only the total concentration of hydrazines, the concentrations of each hydrazine were estimated from the amount of dilution air, the size of the diffusion tube and the temperature of the water bath. Four passive badges each were exposed in three tests: immediately after preparation of the Aerozine-50 mixture, one hour and 24 hours after preparation. The badges were exposed for 12 to 21 minutes, with color developing within 1 to 2 minutes in each test. The 2,4-dinitrobenzaldehyde site responded more rapidly to the vapors than did the vanillin. Table VIIa shows the results of the passive exposures.

Table VIIa
Aerozine-50 Results for Passive Badges

Test	Exposure Time (min)	Badge Site	Color Development	
			Densitometer	Color Wheel
immediate	12	2,4-DNB	47.51	3.5
		vanillin	44.34	3.5
one hour	18	2,4-DNB	48.12	3.5
		vanillin	43.10	3.5
24 hours	21	2,4-DNB	50.49	4.5
		vanillin	40.04	3.5

Active exposures were conducted with the vapor stream generated for 24 hours. Two badges each were exposed for 1 minute and 5 minutes. Table VIIb shows these data.

Table VIIb
Aerozine-50 Results for Active Badges

Test	Exposure Time (min)	Color Development	
		Densitometer	Color Wheel
24 hours	1	26.85	2.5
24 hours	5	37.99	3.0

It is evident from these exposures that the passive and active badges perform as well with a mixture of hydrazine and UDMH as they do with a single hydrazine.

<u>Accelerated Shelf Life Effects</u>

The effects of artificial aging on badge performance was examined. Both passive and active badges were placed in the oven at 40°C for approximately one week. The badges were left in their wrappers while in the oven. Once out of the oven, two "aged" passive badges were exposed to UDMH alongside two badges that had remained in the freezer. The passive badges were exposed to doses of UDMH ranging from 30 to 1500 ppb-hrs. Two oven stored and two freezer stored active badges were exposed to doses ranging from 180 ppb-L

to 13000 ppb-L. Neither the passive nor the active badges showed significant difference in sensitivity to UDMH vapor depending on storage conditions.

Sunlight Exposures

The original passive badge housing was modified by covering the sides, top or LLumar window or adding polypropylene extensions to the face shield in order to determine where the majority of sunlight damage was occurring. One week exposure of the modified badges showed that UV damage was occurring through both the open sides of the badge housing and through the LLumar window. As indicated in Figure 7, the densitometer value for a 40 ppb-hr UDMH exposure was approximately 13.5 units. Therefore, any discoloration due to sunlight which yielded a value greater than the signal-to-noise ratio of 4.5 units was considered unsatisfactory. It was concluded that a larger black faceplate and smaller LLumar window would decrease the UV effects to a satisfactory level. Increasing the thickness of the LLumar from 7 to 21 mil was found to be acceptable; color development on the badge insert card cannot be readily observed through thicker LLumar. New badges were molded and fitted with 21 mil of LLumar.

The sunlight protection of the new, modified badge housings was evaluated in a series of exposures in August at Kennedy Space Center. The new badges were *additionally* modified to determine the extent of sunlight damage to expect when using the badge in outdoor applications. Twelve badges each were modified in the following manner: 1) no modifications, 2) front window covered, 3) two sides covered and 4) two sides and top covered.

Four of each category were placed on a fence in direct sunlight facing south, east and west. The badges with no modifications were exposed to sunlight for 4 consecutive days. They were brought into the lab in the evening and replaced outside the following morning. Densitometer measurements were taken each morning and evening. The control badge was left in the lab for the four day period that the nonmodified badges were exposed to sunlight. Densitometer readings were taken on the control each morning and evening. The rest of the badges were exposed for 1 day. The results of the tests are summarized in Tables VIII and IX.

Table VIII
Multiple Sunlight Exposures for Unmodified Housing

Direction of Badge Face	Day of Exposure	Average Densitometer Value
CONTROL	1	-0.23
	2	-0.20
	3	0.23
	4	0.62
south	1	3.79
	2	6.29
	3	7.90
	4	9.75
east	1	3.72
	2	5.93
	3	7.58
	4	9.38
west	1	3.30
	2	5.40
	3	7.14
	4	8.64

The data in Table VIII indicates that the badges can be used outside for two days. After this time, the intensity of the color development on the badge is greater than the acceptable level. For indoor use, the badge can be worn for at least a week. Because the badges facing south received direct sunlight through the open sides and tops of the badges for the entire day, they developed the most color.

Table IX
One Day Sunlight Exposure for Modified Housings

Housing Modification	Direction of Badge Face	Average Densitometer Value
front window taped	south	3.52
	east	3.45
	west	3.11
two sides taped	south	3.24
	east	3.37
	west	2.89
two sides and top taped	south	2.52
	east	2.72
	west	1.93

Table IX indicates the extent of sunlight effects on the three badge modifications. The badge modified to cover the front LLumar window showed the greatest degree of discoloration regardless of the direction the badge faced. This indicates that more sunlight enters the badge through the sides and top of the housing than through the LLumar window. The magnitude of the response with the front window of the housing taped is similar to that for one day of exposure to sunlight shown in Table VIII. A comparison between Tables VIII and IX indicates that the sunlight effect is not additive.

The evaluation of UV damage to the passive badge insert cards led to several observations and conclusions. When exposed to sunlight, the 2,4-dinitrobenzaldehyde site develops a yellow color which may falsely alarm personnel. A sunlight exposure can be discriminated from a UDMH vapor exposure because of the distribution of color on the reaction site of the badge. During a sunlight exposure, a yellow discoloration develops not only on the exposed portion of the DNB site, but under the contrast ring as well. In a UDMH exposure, color only develops at the exposed portion of the DNB site, not under the contrast ring.

Storage Stability

The passive badges were exposed to doses ranging from 100 to 500 ppb-hours of UDMH. Figure 11 is a comparison of the badges stored in the freezer with those stored at room temperature. The densitometer value determined from the laboratory evaluation at 80 ppb-hours of exposure to UDMH is indicated as the "ideal". Error bars of 30% are represented on the graph. The badges stored in the freezer responded very well to the UDMH vapor over the entire storage period. Badges stored at room temperature indicated a decrease in

sensitivity greater than 30% by 7.5 months after storage.

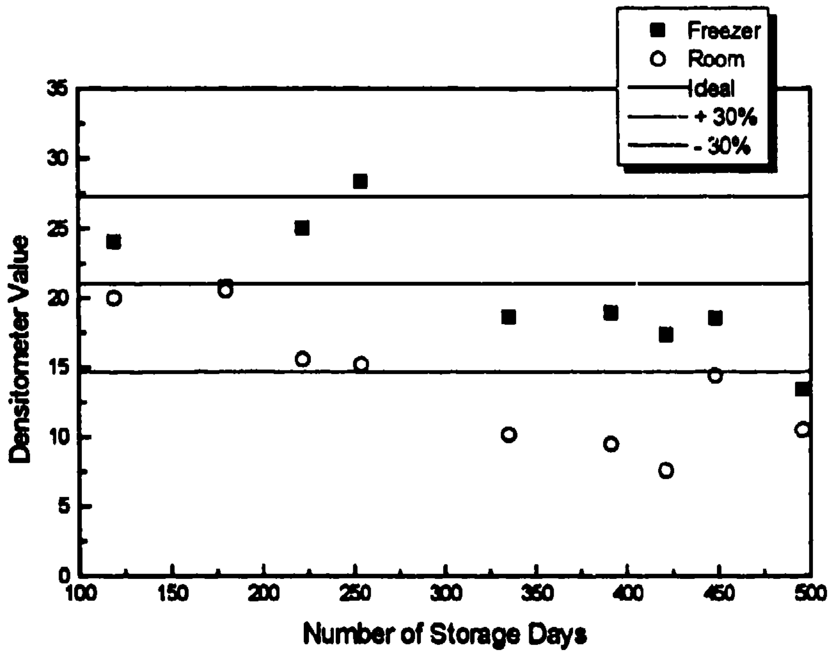


Figure 11. Passive badge response to 80 ppb-hrs of UDMH during storage period.

Figure 12 illustrates the data for active badge exposure after storage. When exposed to 300 ppb-L of UDMH, the badges stored at room temperature indicated a decrease in sensitivity. Almost all responses fell at or below 30% from the ideal which was set at the densitometer value for 130 ppb-L determined from the laboratory evaluation. In contrast, the badges stored in the freezer showed excellent sensitivity throughout the 16 months of storage. Therefore, to guarantee adequate sensitivity to UDMH vapors, the passive and active badges should be stored in the freezer until used. Although not shown here, the badge results as measured with the color wheel were similar for both the passive and active badges.

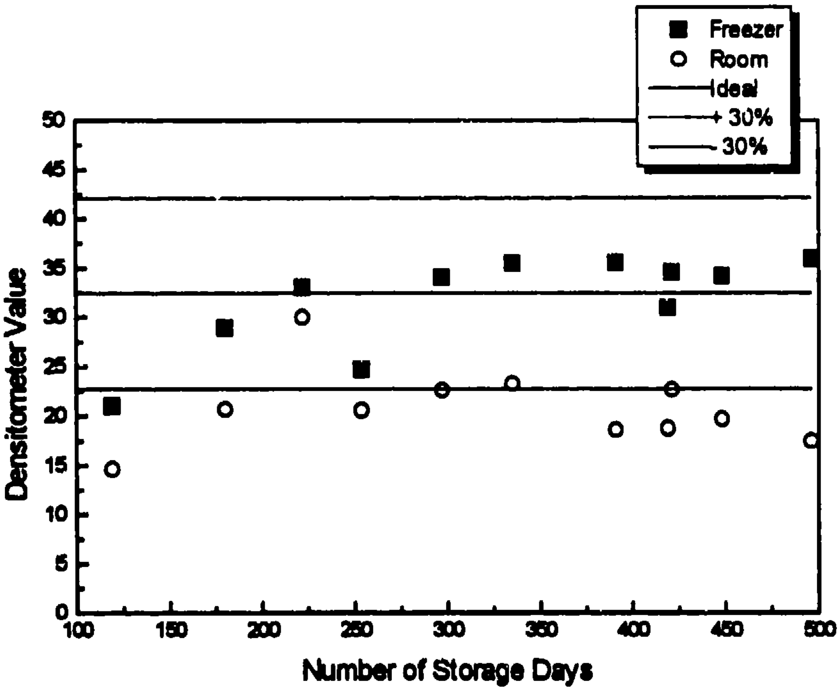


Figure 12. Active badge response to 300 ppb-L of UDMH during storage period.

FIELD TEST

As discussed previously, several methods were used for verification analysis of color badge responses. The detection and quantification limits for each lab analysis method for the verification methods as well as the densitometer and color wheel limits for the colorimetric badges are detailed in Table X. The detection and quantitation limits for the coulometric method were calculated from the standard deviation of blank measurements made with the coulometer. The detection limit was set at three times the standard deviation of the blanks; while the quantitation limit was set at ten times the standard deviation of the blanks. The limits set for the PMA method were provided in the NIOSH method.

The detection limit for the densitometer measurement of the 2,4-dinitrobenzaldehyde site on the colorimetric badge was set using two criteria. First, the Air Force specified a limit of 40 ppb-hrs of UDMH, which is one-half of the required TLV. To account for an acceptable 3:1 noise level, a value of one-third of the densitometer value of a 40 ppb-hrs exposure to UDMH was selected as the first factor. Secondly, sunlight effects were considered in setting the appropriate detection limit. It was determined from various sunlight exposures, that the 2,4-dinitrobenzaldehyde site reached a densitometer color of approximately 5 in two consecutive days of exposure. Because this value approximated a 40 ppb-hr exposure to UDMH, this was was considered the upper limit of acceptable sunlight effects. The average

of the densitometer values from the 40 ppb-hr exposures and from the sunlight exposures gave a detection limit of 4.49, as shown in Table X. The quantitation limit was set at the densitometer value for a 40 ppb-hr UDMH exposure.

The active badge detection and quantitation limits were based on a 5 minute sample of 10 ppb UDMH when sampled at 1L/min. The quantitation limit for the vanllin site on the passive colorimetric badge was based on the densitometer value of the color wheel index 1.0. The detection limit was set at one-third of this value to account for an acceptable signal-to-noise ratio. The detection limits using the color wheel were set at 0.5 color wheel units for all sites.

Table X
Detection and Quantitation Limits for Coulometry, PMA, Densitometer and Color Wheel

Analysis Method	Detection Technique	Detection Limit	Quantitation Limit
coulometry	citric acid samplers	0.31 μg	1.04 μg
PMA	impingers citric acid samplers	2.0 μg	6.7 μg
densitometer	passive badge UDMH site	4.5	13.5
	passive badge MMH/hydrazine site	4.0	12.1
	active UDMH badge	1.8	5.5
color wheel	passive badge UDMH site	0.3	1.0
	passive badge MMH/hydrazine site	0.3	1.0
	active UDMH badge	0.2	0.5

Table XIa shows the number of badges placed in the field for Unlikely Exposure area tests. As was expected, there were no positives greater that the detection limit with eithar the color wheel or the densitometer.

Table XIa
Number of Field Badges For Each Unlikely Exposure Area Test

Location	Total Number of Badges Placed in the Field			
	Single Day Passive	Multiple Day Passive	Sure-Spot Active	Blank
FSA #1	20	10	4	6
FSA #1	30	14	4	10
AF Chem Lab	50	20	18	21
Cx 17 Tower	42	20	16	19
Paint Shop	50	20	20	21

Table XIb indicates the number of citric acid samplers and impingers analyzed for each unlikely exposure area test and the number of positive and negative responses associated. This table shows that the number of positive citric acid samplers and impingers in the Unlikely Exposure area was minimal as compared with the number of negative samples. The Air Force Chemistry lab shows 5 positives by coulometry. Since there were no hydrazines used during this test, the false positives were caused by another compound. The coulometric analysis method is subject to several interferences. Any compound that reacts rapidly with bromine in an acidic solution will produce a false positive with the coulometer itself. Tobacco smoke and sunlight produce false positives with the citric acid samplers. The PMA analysis did not give a significant number of positives.

Table XIb
Citric acid Samplers and Impingers Analyzed by Coulometry and PMA Method for Unlikely Exposure Area Tests

	Total Number of Samples Analyzed		Number of Positive Samples (>DL)	
Location	Coulometry	PMA	Coulometry	PMA
FSA #1	8	2	1	0
FSA #1	8	3	1	0
AF Chem Lab	24	16	5	1
Cx 17 Tower	10	2	2	0
Paint Shop	10	8	2	1

Table XIIa shows the number of badges placed in the field for Highly Probable Exposure areas. There were a number of positive responses with the colorimetric badges using both the color wheel and the densitometer. Table XIIb shows the number of positives for each test as well as the number of colorimetric positives that were verified by the citric acid samplers or impingers. The positives are broken down by single day and multiple day sample status. Multiple day colorimetric badges that gave a positive response were only counted for the first day of the positive response. Colorimetric badges were considered verified if the majority of citric acid samplers and/or impingers analyzed gave positive responses greater than the detection limit for the particular analysis methods. For personnel badges, colorimetric badges were considered verified only if the citric acid samplers corresponding to the same personnel gave positive responses greater than the detection limit. The few single day badges that were not verified by reference methods, were positive only using the color wheel as the measurement method. All showed color of ≤ 1.0 on the color wheel. These badges registered as positive because the industrial hygienists were instructed to consider any color they could visually detect as greater than the detection limit. The densitometer did not register these badges as positive (greater than the detection limit).

Table XIIa
Number of Field Badges For Highly Probable Exposure Area Tests

Location	Total Number of Badges Placed in the Field			
	Single Day Passive	Multiple Day Passive	Sure-Spot Active	Blank
Cx 17 Propellant Load	20	20	0	9
Cx 17 Propellant Load	47	20	12	21
AF Chem Lab	50	20	20	21
AF Chem Lab	50	20	20	21
Cx 40	50	20	20	21

Table XIIb
Verification Status of Colorimetric Badges in Highly Probable Exposure Areas

Location	Total Number of Positive Badges in the Field			
	Dinitrobenzaldehyde			
	Single Day Badges	Verified	Multiple Day Badges	Verified
Cx 17 Propellant Load	3	3	3	3
Cx 17 Propellant Load	21	18	14	14
AF Chem Lab	4	4	3	3
Cx 40	8	4	5	5
FSA #1 Cart Load	12	12	0	0

Passive and active badges that were field tested at Cape Canaveral were returned to NRL for subsequent exposure to UDMH vapors in a controlled environmental setting. The badges were exposed to approximately 30 ppb of UDMH for varying times in order to provide a range of doses. The passive badges were placed in the modified housing used in the field exposures and exposed to UDMH in the glass chamber described previously. Doses ranging from 100 to 4500 ppb-hrs were evaluated. Figure 13 shows a comparison of the passive badges exposed in the laboratory during the initial lab evaluation with those that were field tested and subsequently exposed to UDMH vapors in the lab.

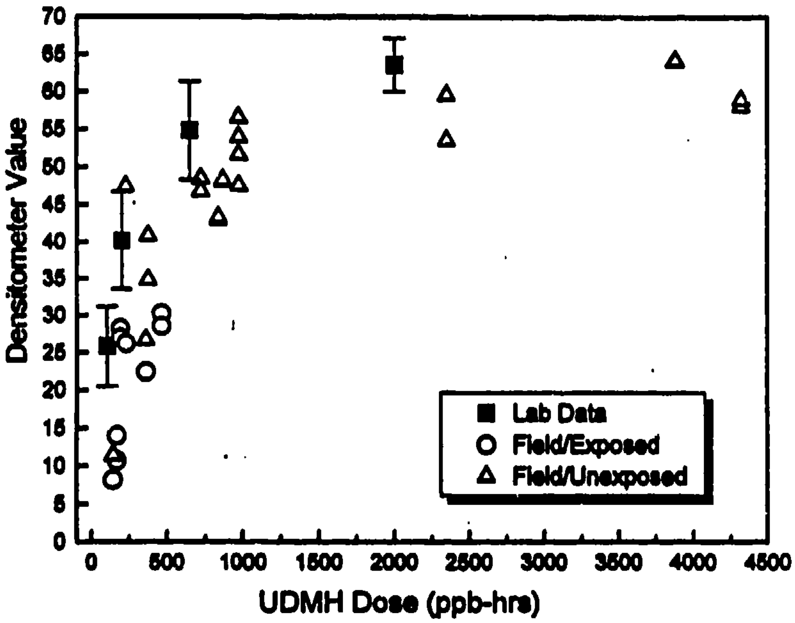


Figure 13. Sensitivity comparison of field tested and laboratory evaluated badges.

In Figure 13, the field test data are divided into two categories; those that were exposed to a field interferent that caused a discoloration, and those that were not discolored during field testing. As evidenced in Figure 13, the passive badges experienced an overall decrease in sensitivity to UDMH vapors after field exposure. However, all field tested badges subsequently exposed to UDMH vapors in the lab responded to the UDMH and developed color. This indicates that the badge chemistry was only partly deactivated by interferents encountered in the field. In addition, there was no significant difference in sensitivity reduction depending upon whether the colorimetric badge had been discolored by a field interferent.

A similar comparison was made with the active badges. Since the sampling rate in the field was 2 l./min, the same rate was used for subsequent laboratory exposure. Although the data is not shown, there was a large decrease in sensitivity after field testing and subsequent lab exposure to UDMH. This was expected and can be easily explained due to the volatility of the chemistry on the paper substrate. Drawing sample through the coated paper with a pump depletes the store of chemicals on the paper substrate, leaving less 2,4-dinitrobenzaldehyde to react with UDMH in subsequent exposures.

It must be noted that there was a time lapse of approximately 1 to 2 months between when the badges were exposed in the field and when they were received at NRL for exposure to UDMH vapor. In addition, the field-exposed badges were not sealed or refrigerated after exposure at Cape Canaveral. To examine the effect those conditions may have had on sensitivity to UDMH vapors, the results from Figure 13 were compared with data from fresh passive badges exposed to ambient conditions for 1, 3 and 5 days and subsequently exposed to UDMH vapor in the NRL lab. Two badge cards were removed from the freezer on Monday, Wednesday and Friday, placed in housings and hung in the lab. At the end of the workweek, the badges were exposed to 200 ppb-hrs of UDMH alongside fresh badges. Exposure to ambient conditions did not cause discoloration of the badges, nor did it affect the sensitivity to UDMH vapors. Therefore, the decrease in sensitivity noted in Figure 13 for the field-exposed badges was due in part to the time lapse and conditions the badges were subjected to after field testing and before exposure at NRL.

CONCLUSIONS

The laboratory evaluation indicated that the dosimeter has the sensitivity and reproducibility required by our sponsors. The dose response of the 2,4-dinitrobenzaldehyde site on the passive badge was not hampered by any interference tested other than extreme heat. Interference effects from passive exposure to heat were to be expected. Low humidity slightly hindered the performance of the passive badge at high doses. Actively, the Sure-Spot badge is useful as a rapid spot test for UDMH. It showed no interference effects. Exposure to low doses of UDMH at high humidity showed a slightly hindered reaction. The shelf life study indicated that passive and active badges can be stored in the freezer for at least 16 months with no degradation of sensitivity to UDMH vapors. Passive badges stored at room temperature responded adequately for 7.5 months after storage, after which time the sensitivity decreased dramatically. Active badges stored at room temperature performed

poorly, showing sensitivity degradation of -30% of "ideal" responses for the entire test period.

In the field test of the hydrazines badge system, the badges performed consistently. Direct sunlight exposures indicated that badge usage in outdoor applications must remain at or below 2 consecutive days. For indoor applications, badges may by used for at least one workweek. The passive badges showed a slight decrease in sensitivity after field exposure which should not hinder reuse of the badges. However, only those badges which have not become discolored should be reused. Active badges are designed for one-time use only as the sampling method depletes the supply of reactant on the substrate, decreasing the sensitivity of the badge dramatically.

Although the citric acid samplers and the impinger/PMA analysis verification methods available for the field test were not as sensitive or specific as the colorimetric badges, they provided results consistent with the colorimetric badges. As noted previously, sunlight is an interferent with the colorimetric dinitrobenzaldehyde chemistry and the coulometric analysis. In testing Unlikely Exposure areas for possible interferences, none were found. Neither solvents, paints nor cross interferences between the hydrazines were noted on the colorimetric badges. There were no false positives or negatives when using the densitometer to measure color development on the field tested badges. A few false positives using the color wheel were noted during two Highly Probable site tests. However, the densitometer did not register these as positives and it must be noted that the color wheel is a subjective form of color measurement for color of 1.0 indices or less.

REFERENCES

1. **American Conference of Governmental Industrial Hygienists:** *TLVs-Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1981*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1981.

2. **American Conference of Governmental Industrial Hygienists:** *1992-1993 Notice of Intended Changes*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1989.

3. **Taffe, P.A. and S.L. Rose:** Hydrazine Detection. U.S. Patent #4,900,681, issued 13 February 1990.

4. **Naval Research Laboratory:** *Laboratory Evaluation of a Colorimetric Hydrazine Dosimeter* by K.P. Crossman, P.T. Carver, J.R. Wyatt, S.L. Rose-Pehrsson and A. Thurow, (NRL Memorandum Report 6668). Washington D.C.: NRL, 1990.

5. **National Institute for Occupational Safety and Health:** *NIOSH Manual of Analytical Methods, Vol.III. 2nd ed.* (DHHEW/NIOSH Pub. No. 77-157c). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977. Method #149.

6. **Wyatt, J.R., S.L. Rose-Pehrsson, T.L. Cecil, K.P. Crossman, N.K. Mehta and R. Young:** Coulometric Method for the Quantification of Low-Level Concentrations of Hydrazine

and Monomethylhydrazine. *Am. Ind. Hyg. Assoc. J. 54(6)*:285-292 (1993).

7. LLumar is a product of Courtaulds Performance Films Industrial Products, P.O. Box 5068, Martinsville, VA 24115, (703) 629-1711. Purchased through Read Plastics, Inc., 12331 Wilkins Ave., Rockville, MD 20852, (301) 881-7900.

8. The densitometer used was a Minolta Chroma Meter CR-300. It is a product of Minolta Camera Co., Ltd., Minolta Corporation Head Office (Meter Div.), 101 Williams Drive, Ramsey, NJ, 07446, (201) 825-4000.

9. **Holtzclaw, J.R., S.L. Rose, J.R. Wyatt and C.M. Hawkins:** Dosimeter for Measuring Exposure to Hydrazine and Hazardous Hydrazine Derivatives. U.S. Patent #4,780,282, issued 25 October 1988.

10. **Rose-Pehrsson, S.L., J.R. Wyatt, K.P. Brenner, P.T. Carver, S.W. Brown, A.R. Thurow and J.C. Travis.** Laboratory Development and Field Evaluation of a Passive Sampling Device for Monomethylhydrazine in Ambient Air. *Am. Ind. Hyg. Assoc. J.* 55(2):149-162 (1994).

11. **National Institute for Occupational Safety and Health:** *NIOSH Manual of Analytical Methods, Vol.III. 2nd ed.* (DHHEW/NIOSH Pub. No. 77-157c). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977. Method #237.